CERTIFICATE

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By the Authority Vested By Part 5 of the United States Code § 552(a) and Part 1 of the Code of Regulations § 51 the attached document has been duly INCORPORATED BY REFERENCE and shall be considered legally binding upon all citizens and residents of the United States of America. *HEED THIS NOTICE*: Criminal penalties may apply for noncompliance.

Document Name: HACH 8000: Oxygen Demand, Chemical Using Reactor Digestion Method

CFR Section(s): 40 CFR 136.3(a)

Standards Body: Hach Chemical Company

APPROVED

Official Incorporator:
THE EXECUTIVE DIRECTOR
OFFICE OF THE FEDERAL REGISTER
WASHINGTON, D.C.

Oxygen Demand, Chemical

DOC316.53.01099

USEPA[1] Reactor Digestion Method[2] — Method 8000

0.7 to 40.0[3] mg/L COD (ULR); 3 to 150 mg/L COD (LR); 20 to 1500 mg/L COD (HR); 200 to 15,000 mg/L COD (HR Plus)

Scope and Application: For water, wastewater; digestion is required

[1] Ranges 3 to 150 mg/L COD and 20 to 1500 mg/L COD are USEPA approved for wastewater analyses (Standard Method 5220 D), *Federal Register*, April 21, 1980, 45(78), 26811-26812.

[2] Jirka, A.M.; Carter, M.J., *Analytical Chemistry*, 1975, 47(8), 1397

[3] The ULR range is not available on the DR 2700 or the DR/2400.

Test preparation

How to use instrument-specific information

The *Instrument-specific information* table displays requirements that may vary between instruments. To use this table, select an instrument then read across to find the corresponding information required to perform this test

Table 1 Instrument-specific information

Instrument	Light shield
DR 3900	LZV849
DR 3800, DR 2800	LZV646

Before starting the test:

DR 3900, DR 3800, DR 2800 and DR 2700: Install the light shield in Cell Compartment #2 before performing this test.
Some of the chemicals and apparatus used in this procedure may be hazardous to the health and safety of the user if inappropriately handled or accidentally misused. Please read all warnings and associated MSDS sheets.
Run one blank with each set of samples. Run all tests (the samples and the blank) with the same lot of vials. The lot number appears on the container label. See *Blanks for colorimetric determination*.
Spilled reagent will affect test accuracy and is hazardous to skin and other materials. Be prepared to wash spills with running water.
Wear appropriate eye protection and clothing for adequate user protection. If contact occurs, flush the affected area with running water. Review and follow reagent MSDS safety instructions carefully.
Store unused (light sensitive) vials in a closed box.
If high chloride samples are being tested, refer to the Alternate reagents section.

Collect the following items:

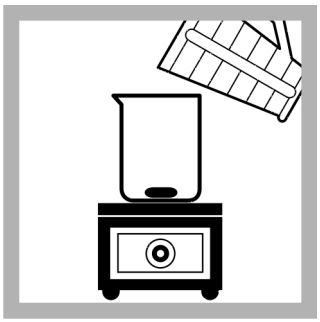
Description	Quantity
Beaker, 250-mL	1
Blender	1
COD Digestion Reagent vials	varies
DRB200 Reactor	1
Light Shield or adapter (see *Instrument-specific information*)	1
Magnetic stirrer and stir bar	1
Opaque shipping container for storage of unused, light-sensitive reagent vials	varies
Pipet, TenSette®, 0.1 to 1.0 mL, with tips (for 200–15,000 mg/L range)	1
Pipet, volumetric, 2.00 mL	2
Pipet Filler, safety bulb	1
Test Tube Rack	2

See *Consumables and replacement items* for reorder information.

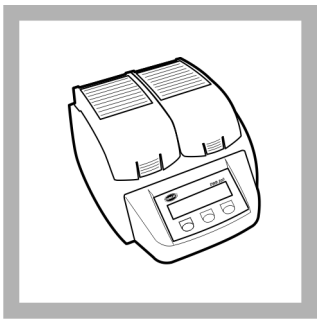
Reactor digestion procedure

1. Homogenize 100 mL of sample for 30 seconds in a blender. For samples containing large amounts of solids, increase the homogenization time.

If the sample does not contain suspended solids, omit steps 1 and 2.

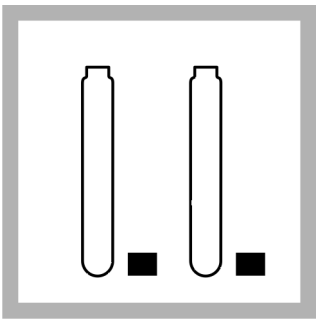


2. For the 200–15,000 mg/L range or to improve accuracy and reproducibility of the other ranges, pour the homogenized sample into a 250-mL beaker and gently stir with a magnetic stir plate.



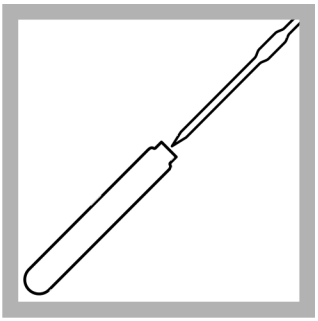
3. Turn on the DRB200 Reactor. Preheat to 150 °C.

See the DRB200 User Manual for selecting pre-programmed temperature applications.



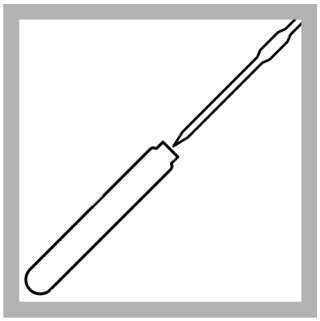
4. Remove the caps from two COD Digestion Reagent Vials. (Be sure to use vials for the appropriate range.)

Reactor digestion procedure (continued)



5. Prepared Sample: Hold one vial at a 45-degree angle. Use a clean volumetric pipet to add 2.00 mL of sample to the vial.

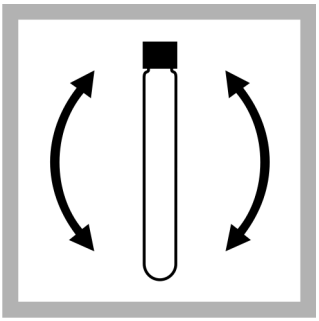
For the 200–15,000 mg/L vials: Use a TenSette® Pipet to add 0.20 mL of sample to the vial.



6. Blank Preparation: Hold a second vial at a 45-degree angle. Use a clean volumetric pipet to add 2.00 mL of deionized water to the vial.

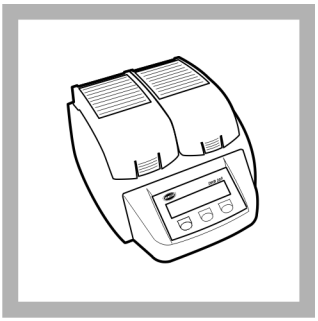
For the 200–15,000 mg/L vials: Use a TenSette Pipet to add 0.20 mL of deionized water to the vial.

7. Cap the vials tightly. Rinse them with water and wipe with a clean paper towel.

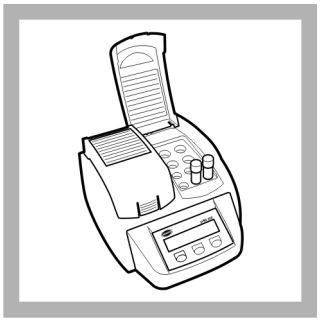


8. Hold the vials by the cap over a sink. Invert gently several times to mix. The sample vials become very hot during mixing.

Insert the vials in the preheated DRB200 Reactor. Close the protective lid.

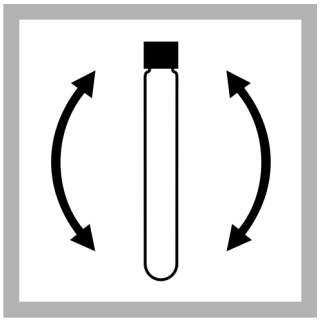


9. Heat the vials for two hours.

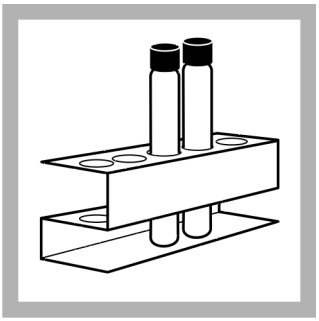


10. Turn the reactor off.

Before removing the vials, wait about 20 minutes for the vials to cool to 120 °C or less.



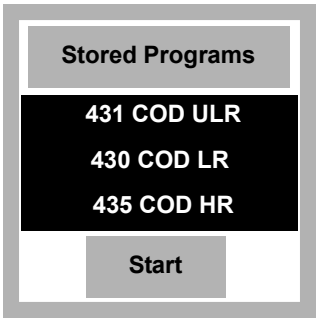
11. Invert each vial several times while still warm.



12. Place the vials into a rack and cool to room temperature.

Proceed to *Colorimetric determination*.

Colorimetric determination

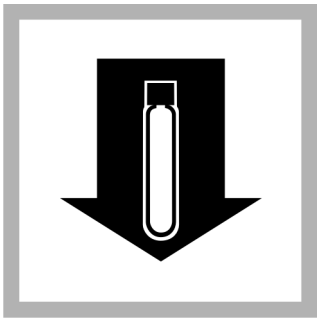


1. Select the test.

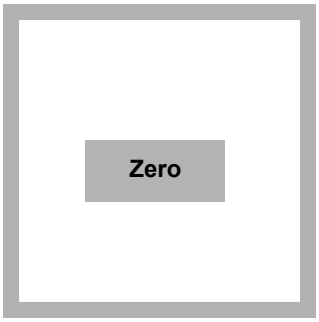
Insert an adapter or light shield if required (see *Instrument-specific information*).

Refer to the user manual for orientation.

2. Clean the outside of the vials with a damp towel followed by a dry one.



3. Insert the blank into the 16-mm cell holder.



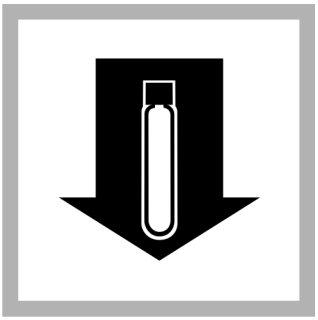
4. **ZERO** the instrument.

The display will show:

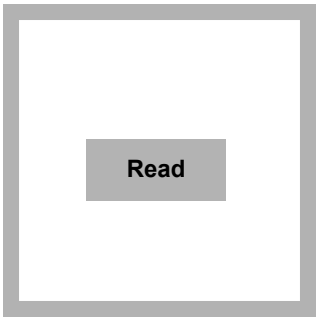
0 mg/L COD

or

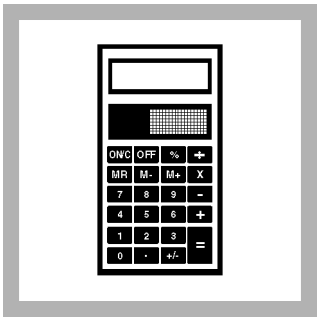
0.0 mg/L COD



5. Insert the sample vial into the 16-mm .



6. **READ** the results in mg/L COD.



7. If using High Range Plus COD Digestion Reagent Vials, multiply the result by 10.

For most accurate results with samples near 1500 or 15,000 mg/L COD, repeat the analysis with a diluted sample.

Blanks for colorimetric determination

The blank may be used repeatedly for measurements using the same lot of vials. Store the blank in the dark.

1. Monitor decomposition by measuring the absorbance at the appropriate wavelength. Refer to the *Range-specific test wavelengths* table.
2. Zero the instrument in the absorbance mode. Use a vial containing 5 mL of deionized water and measure the absorbance of the blank. Record the value.
3. Prepare a new blank when the absorbance has changed by about 0.01 absorbance units.

Interferences

Chloride is the primary interference when determining COD concentration. Each COD vial contains mercuric sulfate that will eliminate chloride interference up to the level specified in *Column 1* of the *Interfering substances* table. Dilute samples with higher chloride concentrations. Dilute the sample enough to reduce the chloride concentration to the level given in *Column 2*.

Note: *For best results, use the low range and ultra-low range test for samples with high chloride concentrations (approaching maximum concentration) and low COD concentrations.*

If sample dilution will cause the COD concentration to be too low for accurate determination, add 0.50 g of mercuric sulfate ($HgSO_4$) to each COD vial before the sample is added.

The additional mercuric sulfate will raise the maximum chloride concentration allowable to the level given in *Column 3*.

Table 2 Interfering substances

Vial range	**Column 1** (Maximum chloride concentration)	**Column 2** (Suggested chloride concentration for diluted samples)	**Column 3** (Maximum chloride concentration with mercuric sulfate)
Ultra Low Range [1] (0.7–40.0 mg/L)	2000	1000	N/A
Low Range (3–150 mg/L)	2000	1000	8000
High Range (20–1500 mg/L)	2000	1000	4000
High Range Plus (200–15,000 mg/L)	20,000	10,000	40,000

[1] Ultra Low Range is not available on the DR 2700.

Sample collection, preservation and storage

- Collect samples in glass bottles.
- Use plastic bottles only if they are known to be free of organic contamination.
- Test biologically active samples as soon as possible.
- Homogenize samples containing solids to assure representative samples.
- Samples treated with sulfuric acid* to a pH of less than 2 (about 2 mL per liter) and refrigerated at 4 °C can be stored up to 28 days.
- Correct the test results for volume additions.

* See *Optional reagents and apparatus*.

Accuracy check

Standard solution method

Note: *Refer to the instrument user manual for specific software navigation instructions.*

Required for accuracy check:

- 1000 mg/L COD Standard Solution

OR

- Potassium acid phthalate (KHP), dried overnight at 120 °C
- Deionized water, organic free
- Class A volumetric flasks
- Class A volumetric pipet

0.7 to 40.0 mg/L range

1. Prepare a 30-mg/L COD standard solution as follows:
   a. Pipet 3.00 mL of the 1000 mg/L standard into a 100-mL volumetric flask.
   b. Dilute to volume with deionized water and mix well.
2. Use 2 mL of the 30 mg/L COD solution in place of the sample. Follow the *Colorimetric determination* test procedure. The result should be 30 mg/L. Refer to the *Standard adjust* instructions in this procedure to adjust the curve with the reading obtained from the standard.

3 to 150 mg/L range

1. Prepare a 100-mg/L COD standard solution as follows:
   a. Pipet 10 mL of the 1000 mg/L standard into a 100-mL volumetric flask.
   b. Dilute to volume with deionized water and mix well.
2. Use 2 mL of the 100-mg/L solution in place of the sample. Follow the *Colorimetric determination* test procedure. The result should be 100 mg/L. Refer to the *Standard adjust* instructions in this procedure to adjust the curve with the reading obtained from the standard

20 to 1500 mg/L range

Use 2 mL of 300 mg/L, 800 or 1000 mg/L COD standards for accuracy check.

200 to 15,000 mg/L range

1. Prepare a 10,000-mg/L COD standard solution as follows:

   a. Dissolve 8.500 g of dried KHP in 1000-mL of organic-free deionized water.

2. Use 0.2 mL of the 10,000 mg/L COD solution in place of the sample. Follow the *Colorimetric determination* test procedure. The result should be 10,000 mg/L (after multiplying by 10). Refer to the *Standard adjust* instructions in this procedure to adjust the curve with the reading obtained from the standard.

Standard adjust

1. To adjust the calibration curve using the reading obtained with the standard solution, navigate to Standard Adjust in the software: **OPTIONS>MORE>STANDARD ADJUST**.

2. Turn on the Standard Adjust feature and accept the displayed concentration. If an alternate concentration is used, enter the concentration and adjust the curve to that value.

Alternate reagents

Mercury-free COD2 Reagents can provide a mercury-free testing option for non-reporting purposes. For process control applications, COD2 Reagents will eliminate mercury waste and save on disposal costs. These reagents are fully compatible with test procedures and calibration curves programmed into the spectrophotometer. Determine chloride and ammonia for accurate results.

Important Note: *COD2 reagents are not approved for USEPA reporting purposes. Because COD2 reagents do not contain mercury as a masking agent, they exhibit a positive interference from chloride. Request a copy of the COD2 Reagent Vial Information Brochure, Lit. No. 1356, for more information about specific applications.*

Method performance

Program	Standard	Precision 95% Confidence Limits of Distribution	Sensitivity Concentration change per 0.010 Abs change
430 (Range, 3–150 mg/L)	80 mg/L COD (Low Range)	77–83 mg/L COD	3 mg/L COD
431 (Range, 0.5–40.0 mg/L)	30 mg/L COD (Ultra Low Range)	28.8–31.2 mg/L COD	0.5 mg/L COD
435 (Range, 20–1500 mg/L)	800 mg/L COD (High Range)	785–815 mg/L COD	23 mg/L COD
435 (Range, 200–15,000 mg/L)	8000 mg/L COD (High Range Plus)	7850–8150 mg/L COD	230 mg/L COD

Summary of method

The results in mg/L COD are defined as the milligrams of O_2 consumed per liter of sample under the conditions of this procedure. The sample is heated for two hours with sulfuric acid and a strong oxidizing agent, potassium dichromate. Oxidizable organic compounds react, reducing the dichromate ion ($Cr_2O_7^{2-}$) to green chromic ion (Cr^{3+}).

When the 0.7–40.0 or the 3–150 mg/L colorimetric method is used, the amount of Cr^{6+} remaining is determined. When the 20–1500 mg/L or 200–15,000 mg/L colorimetric method is used, the amount of Cr^{3+} produced is determined. The COD reagent also contains silver and mercury ions. Silver is a catalyst, and mercury is used to complex chloride interferences.

Test results are measured at the wavelengths specified in the *Range-specific test wavelengths* table.

Table 3 Range-specific test wavelengths

Range in mg/L COD	Wavelength
0.7 to 40.0 mg/L[1]	350 nm
3 to 150 mg/L	420 nm
20 to 1500	620 nm
2000 to 15,000 mg/L	620 nm

[1] Not available on the DR 2700

Consumables and replacement items

Required reagents

Description	Quantity/Test	Unit	Catalog number
Select the appropriate COD Digestion Reagent Vial:			
Ultra Low Range, 0.7 to 40 mg/L COD	1–2 vials	25/pkg	2415825
Low Range, 3 to 150 mg/L COD	1–2 vials	25/pkg	2125825
High Range, 20 to 1500 mg/L COD	1–2 vials	25/pkg	2125925
High Range Plus, 200 to 15,000 mg/L COD	1–2 vials	25/pkg	2415925
Water, deionized	varies	4 L	27256

Alternate reagents[1]

Description	Quantity/Test	Unit	Catalog number
Select the appropriate COD Digestion Reagent Vial:			
COD2, Low Range, 0 to 150 mg/L COD	1–2 vials	25/pkg	2565025
COD2, High Range, 0 to 1500 mg/L COD	1–2 vials	25/pkg	2565125
COD2, High Range, 0 to 1500 mg/L COD	1–2 vials	150/pkg	2565115
COD2, High Range Plus, 0 to 15,000 mg/L COD	1–2 vials	25/pkg	2834325
COD Digestion Reagent Vials, 3 to 150 mg/L COD	1–2 vials	150/pkg	2125815
COD Digestion Reagent Vials, 200 to 1500 mg/L COD	1–2 vials	150/pkg	2125915
COD Digestion Reagent Vials, ULR 0.7-40.0 mg/L	1-2 vials	150/pkg	2415815
COD Digestion Reagent Vials, HR plus,200-25,000 mg/L	1-2 vials	150/pkg	2415915

[1] These reagents are not approved for USEPA reporting purposes. Request a copy of the COD2 Reagent Vial Information Brochure, Lit. No. 1356, for more information about specific applications.

Required apparatus

Description	Quantity	Unit	Catalog number
Blender, 2-speed, 120 VAC	1	each	2616100
OR			
Blender, 2-speed, 240 VAC	1	each	2616102
DRB200 Reactor, 110 V, 15 x 16 mm	1	each	LTV082.53.40001
OR			
DRB200 Reactor, 220 V, 15 x 16 mm	1	each	LTV082.52.40001
Pipet Filler, safety bulb	1	each	1465100
Pipet, Volumetric, Class A, 2.00 mL	1	each	1451536

Recommended standards and apparatus

Description	Unit	Catalog number
Beaker, 250-mL	each	50046H
COD Standard Solution, 300-mg/L	200 mL	1218629
COD Standard Solution, 300-mg/L	500mL	1218649
COD Standard Solution, 800-mg/L	200 mL	2672629
COD Standard Solution, 1000-mg/L	200 mL	2253929
Oxygen Demand Standard (BOD, COD, TOC), 10-mL ampules	16/pkg	2833510
Pipet, TenSette®, 0.1 to 1.0 mL	each	1970001
Pipet Tips, for TenSette Pipet 1970001	50/pkg	2185696
Pipet Tips, for TenSette Pipet 1970001	1000/pkg	2185628
Potassium Acid Phthalate, ACS	500 g	31534
Stir Bar, 28.6 x 7.9 mm	each	2095352
Stirrer, Electromagnetic, 120 VAC, with electrode stand	each	4530001
Stirrer, Electromagnetic, 230 VAC, with electrode stand	each	4530002
Test Tube Rack, 16 mm	each	1864100
Wipes, Disposable	70/pkg	2096900

Optional reagents and apparatus

Description	Unit	Catalog number
Balance, analytical, 80 g capacity, 115 VAC	each	2936701
Flask, volumetric, 1000 mL Class A	each	1457453
Flask, volumetric, 100-mL Class A	each	1457442
Mercuric Sulfate	28 g	191520
Pipet, volumetric, 3-mL, Class A	each	1451503
Pipet, volumetric, 10-mL, Class A	each	1451538
Sulfuric Acid, conc	500 mL	97949
Wastewater Influent Standard for mixed parameters NH_3–N, NO_3–N, PO_4, COD, SO_4, TOC	500mL	2833149
Wastewater Effluent Standard, for mixed parameters NH_3–N, NO_3–N, PO_4, COD, SO_4, TOC	500mL	2833249
Weighing Paper, 76x76 mm	500/pkg	1473800
Finger cots	2/pkg	1464702
Gloves, chemical resistant 9-9 ½"[1]	1 pair	2410104
Safety goggles, vented	each	2550700
EZ COD™ Recycling Service with 5-gal[2] bucket–mail back[3]	each	2895405
EZ COD™ Recycling Service with 5-gal bucket–pick up[3]	each	2895405P

[1] Other sizes are available

[2] 20 and 55 gal are available.

[3] ez COD available to U.S. customers only

FOR TECHNICAL ASSISTANCE, PRICE INFORMATION AND ORDERING:
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Outside the U.S.A. – **Contact the HACH office or distributor serving you.**
On the Worldwide Web – **www.hach.com**; E-mail – **techhelp@hach.com**

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